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Improvements in the Lead-Acid Battery for Load Leveling Applications FY78 Summary Report

A. C. SIMON, S. M. CAULDER, C. P. WALES, AND R. L. JONES

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May 2, 1979



For the U.S. Department of Energy, Energy Storage Systems Division
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IMPROVEMENTS IN THE LEAD-ACID BATTERY FOR LOAD LEVELING
APPLICATIONS
(EC-76-A-31-1003A002)

Extended Abstract

The lead-acid battery has many advantages as an energy source, but suffers ultimately from low energy density. A review of the battery constituents shows that the only area where research might lead to pronounced improvement is the active material. It is well known that active material utilization in commercial batteries may be as low as 30% and seldom exceeds 50%.

Low utilization of active material has long been considered an inescapable fact of lead-acid battery operation, but findings from the present research indicate that substantial improvement may in fact be possible.

The new prospect for increased lead-acid battery efficiency derives from the NRL discovery that low active material utilization is largely caused, in the positive plate, by the presence of an electrochemically inactive PbO_2 polymorph. The percentage of this species, which appears to be created in part in the initial plate formation, increases with cycling and progressively reduces the active material efficiency. Ordinary x-ray spectroscopy will not differentiate between the two forms, but nuclear magnetic resonance shows that the electrochemically active PbO_2 structure incorporates a proton entity lacking in the inactive PbO_2 . This has been confirmed by special x-ray and neutron diffraction techniques, which are now being applied to define the exact locations of the O and H atoms in the active versus inactive PbO_2 forms. Such structural information, in addition to helping explain the difference in electrochemical behavior, should also provide insight concerning how active PbO_2 may be produced and maintained in preference to the inactive form.

A second area of promise for improved active material performance lies in the revelation by NRL that positive plate active material in cyclic operation seems invariably to change over to a characteristic "coralloid" structure,

regardless of previous treatment, paste formulation, or method of formation. This structure consists of interconnected branches and tortuous voids, and there is reason to believe that if the branch diameter were reduced, the active material capacity and perhaps cycle life would be improved. There appears to be a high possibility of accomplishing this, moreover, since certain battery factors are already known that affect the coralloid dimensions; Pb-Ca grids, for example, cause the branch diameter to increase.

In addition to the structural investigations, comprehensive research is being directed to an understanding of physical and chemical environments produced in the plate active material during service, since it is these environments which finally determine what phases and structures will prevail. These studies are based on laboratory cycling experiments where such parameters as current density, cycling regime, electrolyte specific gravity and temperature are varied, but they also include examination of plates from production line and service problem batteries supplied to NRL by various battery manufacturers under an ILZRO-NRL cooperative program. In each case, the goal is to identify the factors which correlate with occurrence of electrochemically active phases in the plate active material.

IMPROVEMENTS IN THE LEAD-ACID BATTERY FOR LOAD LEVELING APPLICATIONS
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FY78 Summary Report

INTRODUCTION

Since this investigation has been in progress for three years, it would seem advisable to review the principal objectives and accomplishments in order to provide continuity, and to explain some of the directions that the research has taken in order to demonstrate their relevance to the attainment of the main goals.

It is probably redundant to review reasons for investigating the lead-acid battery. The fact is, however, that the lead acid battery, because of its relatively low price, reliability, and the plentiful supply of its principal raw material (lead), is the only battery now available for anticipated energy storage applications. In addition, this battery is now produced in large size cells, and further scale up to the size anticipated for load leveling or energy storage does not appear to offer any problems other than those which accompany any model changeover.

So dependable has the lead-acid battery become in its usual applications that the belief has arisen erroneously among laymen that no further investigation of this battery is necessary or desirable. As a matter of fact, while there has been a slow but continuous improvement in lead acid battery performance and dependability over the long period of its existence, these improvements have mainly been limited to better engineering of parts and the use of improved construction materials derived largely from research in other areas. Considering the long time that this battery has existed, there has been relatively little effort to understand the complex chemistry upon which the successful operation of the battery system is based. This lack of research arises partly from the fact that this is a highly competitive and cost conscious industry which does not encourage research expenditure, and partly from the fact that it has been possible in the past to produce a product, without extensive research, that has been adequate for most prior applications.

Note: Manuscript submitted March 6, 1979.

The use of the lead acid battery for large scale energy storage and for road-going electric vehicles will place much greater demands upon its performance, and it has become increasingly evident that the required increase in performance can not be expected from engineering changes alone. Clearly, more emphasis must be placed upon understanding the fundamental battery processes if the lead acid battery is to be successful in these new and critical applications.

FACTORS AFFECTING THE COMPETITIVE POSITION OF THE LEAD-ACID BATTERY

In determining whether the lead-acid battery can compete as an effective means of energy storage against present and proposed alternative systems, several factors must be considered:

The first is energy density, or the weight of battery required to store a unit amount of electricity, usually expressed a watt hrs/lb or watt hrs/kilogram. In this respect, the lead-acid battery is notoriously bad, having the unenviable position of possessing the lowest energy density of any commercial battery. Fortunately, in batteries for stationary applications, such as for energy storage, this is not as important a consideration as would be the case for automobile or truck propulsion, where a decided penalty is paid for low energy density. However, it is evident that any improvement in energy storage without a corresponding weight increase would improve the competitive position of the lead-acid battery and make it more desirable for applications of the future.

A second factor concerns life and reliability. The lead acid battery shows up well in this comparison, as such batteries can be made with proven life in excess of twenty years or a capability for thousands of charge-discharge cycles. Although these characteristics can be obtained, it is unfortunately not without penalty. The increased thickness of plates, the thicker separators and the necessary fiberglass mats or other wrappings, all add up to reduced capacity for a given size and weight of battery. The heavy wrappings are to prevent the softening and dislodgment of the active materials, and the thick plates are required to insure sufficient grid material for support of the active material and for current collection over the long service period during which corrosion is constantly reducing the grid's effective thickness, strength and conductivity.

Another factor that must be considered is how well the battery retains an applied charge during periods of no use, and also what portion of the original capacity can be retained by the battery after a period of charge-discharge cycling. It is an unfortunate fact concerning all types of batteries that the capacity to store electricity and convert it subsequently to useful work is continuously reduced as the battery is cycled. The charge already within any type of battery at any given time of its life is also slowly lost while the battery stands unused.

Batteries are also compared on the basis of cost per kilowatt and cost per kilowatt hr. Costs per kilowatt are based upon the voltage and current that a battery can be expected to produce during the first or an early discharge. Such a figure has little significance as a comparison, except as to initial cost. On the other hand, the total number of kilowatt hrs put into and removed from a battery during its useful life gives not only a measure of the total costs, but also the efficiency of the process.

These cost factors depend not only upon the service life of the battery but also upon its original cost to manufacture. While the figures presented for some of the proposed batteries are only projections, the figures for the lead-acid battery are based on actual data and have proven considerably lower than for any other battery now in production.

Although large amounts of energy can be stored in a battery, it can be neither stored nor removed at rates as high as are desirable. Neither is it possible to get all of the electricity back that was put in, and the higher the rate of charging, the lower is the electrical return. The ratio of electrical input to electrical return is known as charge efficiency, and the rate at which charge can be put into the cell is termed its charge acceptance. Both of these factors vary with different types of batteries.

The above list, while not complete, represents the principal points to be considered in comparing battery systems and also serves to indicate the various ways that batteries are imperfect and where improvement is needed. While some of these factors may appear unrelated, investigation has shown that they are merely different manifestations of the same basic imperfections in battery chemistry.

In considering the problem of energy density, the lead-acid battery materials are themselves very heavy. The lead compounds comprising the active material and the lead alloys required to give the current collector the necessary corrosion resistance have very high densities. Although the actual weight percentages of the various constituents may vary with the type of construction used (as required for different applications), generally the electrolyte constitutes about 20% of the total battery weight, the active material about 40%, the grids about 27% and the container, separators, internal cell connectors and terminals make up the remaining 13%.

Nothing can be done about the weight of the electrolyte. Almost all of it is required for the cell reaction and any remainder is required to furnish conductivity between the plates when they are in a discharged condition. A large number of experiments have demonstrated that the presently used specific gravities of acid are the best compromise of factors such as viscosity, conductivity, heat transfer, diffusion, grid corrosion and resistance to freezing.

There have been numerous attempts to reduce the weight of the grids, since these represent about a fourth of the total weight of the battery and yet contribute nothing to the cell reactions that furnish energy. Such grids are unfortunately required, both as a support for the active material and as internal current collectors. In recent years, computer studies have produced grid designs that appear to offer the best approach to uniform current distribution throughout the plate, but there has been very little reduction in grid weight, because the conductivity of the active material is so low in the discharged condition that numerous grid wires, of rather close spacing, are required to insure that current is carried to and from all parts of the active material. The inability to provide a corrosion proof material for this function also requires the presence of a greater amount of lead than is required just for strength and conductivity. Although many grid alloys have been tried, most have proven unsuccessful for any of a number of reasons and all investigators have been forced to employ lead as a major constituent of whatever alloys they tested. There exists the possibility that greater corrosion resistance could be obtained by a protective overcoat of some material such as titanium, or even that a better conductor such as aluminum could be used as a grid, if properly protected. At the present time, none of these ideas appear practical, especially if the low cost and materials availability of the lead-acid battery is to be preserved.

Although the active material makes up but 40% of the battery weight, it represents 100% of the useful energy that can be either stored in or removed from the system. Since it is a well known fact that less than 50% of the active material is presently utilized, it is obvious that any increase in this utilization would result in an increase in the energy density. As a theoretical possibility, if the utilization could be made high enough, the energy density could be doubled.

As for the remaining 13% (comprising the separators, internal connectors, terminals and container), recent improved plastics and separators appear to have resulted in about as much improvement in these materials as can reasonably be expected (at least as far as weight is concerned) and because of the corrosion problem, internal connectors and terminals will probably remain at their present weights.

NRL—INDUSTRY COOPERATION

The above makes clear that the only areas of investigation offering real possibilities of major improvement in this battery system are those that concern the active material and the grid and it appeared that the most productive effort that could be made by NRL would be in determining the mechanisms of active material failure and grid corrosion so that greater utilization and longer life could be imparted to the active material and more corrosion resistant grids could be developed. Rather than engage in Edisonian type testing of innumerable grid alloys or make

up a variety of paste compositions for life cycling, we sought to define the correlation between corrosion resistance and alloy structure, and to define the effect of phase changes and the migrations of added elements into and through the corrosion layer. In the same manner, we have attempted to correlate changes in micro and atomic structure with the degree of active material utilization, cycle life, and capacity. By studying characteristics of the active material provided by the various cooperating battery companies and by being able to study the changes in these materials produced by various types of service regimes, we have been able to determine what characteristics batteries of different methods of manufacture share in common, what is usual and what is uncommon behavior, what is desirable and what is not, and how the characteristics of the plate vary with various types of operation.

Thus, because of the unstinted cooperation of battery manufacturers both in the U.S. and abroad, we have been able to accumulate and investigate a far larger number of samples than would have been possible through our own unaided efforts. In addition, these samples are far more representative of actual battery manufacture than would be the case of laboratory samples. The sophisticated equipment available at NRL for sample investigation, identification and analysis of trace elements, micro and atomic structure determination, coupled with special techniques developed at NRL specifically for battery examination have enabled us to make the best possible use of this cooperation of the battery manufacturers and to obtain a better overall picture of battery mechanisms than would be possible to an individual manufacturer. Naturally, much of this overall background has required privileged and proprietary information that we have made every effort to keep confidential in order to preserve this relationship with the manufacturers.

The remaining discussion will concern what has been accomplished and what is proposed for future study within the framework of this research grant.

PAST ACCOMPLISHMENTS OF THIS INVESTIGATION

The investigation of means to (a) increase utilization of the active material, (b) reduce or eliminate capacity loss during charge-discharge cyclic operation, and (c) prevent disintegration of the active material are considered as the primary aims of our research. As mentioned previously, the underlying causes of these phenomena are inter-related and it is difficult to discuss them as separate occurrences. It should be noted that, while grid corrosion investigation is being carried out at NRL, it is not a part of the investigation being discussed here as accomplished or proposed for future work. The single exception is our consideration of the possible effects of elements escaping from or through the grid corrosion product, in regards to their effect on the properties of the active material; a very good example of an element having such an effect is antimony.

FACTORS LIMITING ACTIVE MATERIAL UTILIZATION

Various mechanisms have been proposed to explain why the active material is not fully utilized. For the present, we will consider only those that might occur in the first discharge.

(1) The fact that lead in the negative active material and lead dioxide in the positive are both converted to lead sulfate of much lower conductivity offers the possibility that, as the resistance continues to increase, the remaining lead or lead dioxide becomes isolated so that further reaction is prevented.

(2) Either the crystal size or crystal morphology of the lead sulfate allows formation of a passivating layer on the lead dioxide or lead that prevents further reaction.

(3) The formation of lead sulfate crystals clogs the pores of the plate so that diffusion of the electrolyte is prevented and the reaction remains incomplete for lack of available sulfate ion.

(4) In the dissolution process accompanying the formation of lead sulfate, complete loss of contact occurs either by the formation of lead sulfate crystals that are of a size and shape so that they do not sufficiently contact one another or by the gradual dissolution of lead dioxide so that individual crystals, becoming of smaller size, lose contact with one another.

(5) A portion of the PbO_2 first formed is electrochemically inactive and does not convert to $PbSO_4$.

Actually, none of the above is entirely correct or incorrect, as the cause of incomplete utilization of the active material. Which mechanism predominates and to what extent has been found to depend upon how the battery is being operated and whether we are describing conditions as they exist at the first or at much later discharges.

The fact that, in the initial cycles, x-ray and optical examination show that there is no residual lead sulfate when the plate is recharged indicates that contacts between all of the sulfate crystals formed during discharge must have been adequate or this material would not have reconverted to lead dioxide. While the pores in a freshly formed plate are much smaller than those that appear in later cycles, microscopic examination has shown that, at low rates of discharge, lead sulfate forms as isolated crystals within these pores and leaves the surrounding lead dioxide uncovered for continued dissolution, so that the idea of passivation seems unlikely. At the same time that compact crystals of lead sulfate are growing, the surrounding less compact lead dioxide is dissolving, so that the pore size is increasing (1). At higher rate of discharge, the surface of the PbO_2 becomes covered with scale-like deposits of lead sulfate crystals which might be considered as passivat-

ing, except for the fact that SEM examination reveals numerous areas where the layer appears to be incomplete. If the plate is very completely discharged at very low rate, the active material is almost entirely converted to lead sulfate, but there will be a few patches of PbO_2 still present that indicates that mechanism (4) above may have been responsible. In addition, cross sections of the lead sulfate crystals show numerous PbO_2 particles that appear to be very small and not interconnected within the crystal. The very large number of such particles and their discontinuous and random occurrence within the structure of the lead sulfate crystal, together with evidence still to be discussed, has led to the conclusion that these particles represent inactive PbO_2 , which has been released from the bulk PbO_2 during its dissolution, and has then settled on the surfaces of the growing PbSO_4 crystals, to become subsequently engulfed in the crystal's continued growth (2).

It was found that this embedded PbO_2 contributes to the ease of the PbSO_4 reversion to PbO_2 on the following recharge. Not only do these numerous encapsulated particles decrease the resistance across the lead sulfate crystal, but they lead to lattice dislocations that increase the ease of solution. They also have been found to act as nucleation centers for the reversion to lead dioxide. Microscopic examination has revealed that the lead sulfate crystal begins its conversion to PbO_2 upon this already existing inactive PbO_2 wherever it is exposed. The process continues at other sites on the crystal as each new inactive PbO_2 particle is exposed by dissolution of the PbSO_4 surrounding it. The resulting mechanism does not produce a PbO_2 structure that in any way resembles that of the PbSO_4 from which it was formed. It can be seen, however, that this mechanism reintroduces the inactive PbO_2 particles into the structure of the active PbO_2 . Naturally, in the dissolution process, all of the inactive PbO_2 does not fall on PbSO_4 crystals to become subsequently attached, so that a considerable portion escapes as loose sediment. It would seem that, by continued charge and discharge, almost all of the inactive particles would be lost in this manner. As will be discussed later, it appears, however, that the inactive form of PbO_2 increases as cycling continues, probably by a portion of the formerly active PbO_2 becoming inactive.

From these facts and others made in the course of the investigation, it would appear that the presence of inactive PbO_2 is the principal reason that the utilization of the active material is so low, at least in the case of the positive plate.

INACTIVE PbO_2 STUDIES

Investigation made with differential thermal analysis and mass spectrography revealed a difference in water content of electrochemically prepared and chemically prepared PbO_2 , and also a difference in the decomposition products, indicating a subtle difference in atomic structure (3). A nuclear magnetic resonance study indicated the presence of

a proton species other than water in the electrochemically prepared form of PbO_2 that was not present in the chemically prepared form. Subsequent nuclear magnetic investigation showed that an increasingly large amount of material giving the same signals as the chemically prepared form of PbO_2 was appearing in the active material, as cycling was increased. The logical supposition from this work was that the electrochemically inactive form was the same as, or had a structure very similar to, the chemically prepared form.

Since the chemically prepared PbO_2 was already known to be electrochemically inactive, and since PbO_2 can be pressed into a dense plate with almost metallic properties, it was proposed that this material might serve as the cell wall in a bipolar cell (4). Attempts were made to test this idea but it was found that the chemically prepared form of PbO_2 did react to a slight extent and nuclear magnetic studies showed that a small amount of electrochemically active PbO_2 was present in the chemically prepared form. As we have not as yet found a way to separate the active from the inactive form or to prepare either in the pure state, this part of the investigation has been shelved.

The observation was made that the active material made from tetrabasic lead sulfate had a dense shell of PbO_2 around the tetrabasic lead sulfate crystals after formation that was quite different in appearance from the material on the interior of the crystals or that formed from other lead sulfates. It was further noted that this material resisted reduction to lead sulfate during discharge of the plate and remained as PbO_2 , outlining the shape and position of the tetrabasic lead sulfate crystals present in the original paste. Although this network eventually disappeared after repeated charge-discharge cycles, there was at the same time an increase in the concentration of small PbO_2 particles found in the interior of the lead sulfate crystals, leading to the conclusion that, although the network had broken up so as to be no longer discernible, the inert particles of which it was composed were mostly still present (5).

Since tetrabasic lead sulfate is the most basic of the series of lead sulfates, it was reasoned that this indicated that a condition of higher pH favored the formation of an electrochemically inactive form of PbO_2 . Since a similar condition could conceivably exist at the center of a plate during formation and even during cycling, it was a condition of an earlier proposal (4) that the effect of flowing electrolyte through the positive plate would be studied, to see if the electrochemically active portion could be increased. Although there had been unsuccessful attempts in the past to force electrolyte through the plates and it was definitely known that this could not be done with a formed but uncycled plate, it was felt that results would be more successful once the coralloid structure developed. Under SEM and optical microscopy the coralloid structure appeared to be more open and porous than the structure immediately after forming. This coralloid structure will be discussed more fully in a later section. The result

of considerable experiment in this direction has led to the conclusion that percolation, rather than flow, is possible through the negative plate but that the positive plate remains impermeable up to pressures where failure of the active material structure occurs. The apparently open coralloid structure, as it is seen with the SEM, must not extend as open channels completely through the plate but must terminate as dead ends after comparatively short distances. Attempts to make positive plates with a different type of structure were successful but after a few cycles they converted to the coralloid type. Even in their original state, however, deterioration was rapid. Based on these experiments, we have concluded that any reports of success with electrolyte flowing through the positive plates were based on the use of plates with cracks or other imperfections rather than by true flow through the pores. This line of investigation has therefore been abandoned. One interesting result of the tests, however, was that increased discharge rates were obtained, based solely on rapid electrolyte flow across the surface of the plates.

Another idea that we proposed was that some measure of the extent of (6) inactive PbO_2 present in the active material and reasons for its occurrence might be obtained by plating PbO_2 onto platinum, using a variety of plating conditions, and by making quantitative discharges combined with weighed deposits, obtain a quick method for determining how much inactive PbO_2 was present for a given set of conditions. This idea was also beset by many difficulties. Under certain sets of conditions, PbO_2 adherence was very poor and it was also found difficult to get reproducible reduction of the PbO_2 . As a consequence, the results were unreliable and could not be repeated with any precision. After considerable experimentation, this line of investigation was also abandoned.

CORALLOID STRUCTURE

Mention has been made of the coralloid structure. Combined optical microscopy and SEM examination has revealed that after a few cycles, the positive plate microstructure changes from a dense, very fine pored structure, into an interconnected, apparently porous structure, in which the pores are quite large (2, 7). From a theoretical standpoint, this structure appeared to be beneficial and the connected, densely packed members of the coralloid structure seemed to furnish improved conductivity and strength to the active material, while the porous nature of the structure should have been ideal from the standpoint of electrolyte flow.

As has already been stated, this structure is not as permeable as first appearances seemed to indicate. Apparently it must consist of more or less closed cells. Also, the diameter and density of the connecting members of this structure are such that a great deal of PbO_2 is made unavailable for reaction, if discharge is made at a rate sufficient that a passivating film of PbSO_4 covers most of the surface.

PROGRESS MADE THIS YEAR (1978)

CORALLOID STRUCTURE

We previously reported that the coralloid structure is formed, after a few cycles, in all pasted positive plates, regardless of the manufacturer, methods of pasting or curing, or the paste formulation (7). Until recent investigation of tubular battery plates, we were not aware that the same phenomenon occurred in that case.

Because of the possibility that tubular positive plates might be used in the BEST facility or even eventually in larger installations, it was deemed advisable to examine this type of plate to see what might appear as operational problems.

Tubular positives are made by quite a different process than that used for pasted plates. Instead of employing a grid into which a wet mass (made from lead oxide and sulfuric acid) is pasted, a spline and tube construction is used. The tubes are open cylinders of woven fiber glass or other suitable material with the desired degree of porosity. The lead alloy splines are connected together in the manner of a comb, and around each is placed one of the porous cylinders. A dry mix of lead oxide and other materials is then introduced to fill the space between cylinder wall and the central spline, this process being considerably aided by vibration. When the tubes are filled, the bottoms (or in this case, the tops, since the plate is inverted during filling) are stoppered by a suitable plug. The outside is then sprayed with dilute sulfuric acid to promote the formation of lead sulfate that will prevent the escape of oxide dust during subsequent assembly steps. Before formation, the plates are soaked in acid for a suitable length of time to convert a considerable portion of the lead oxide into basic or normal sulfate.

This process is completely different from that employed in the production of pasted plates. There is no mixing of the oxide with acid to form a paste, and there is no curing before formation. A very important factor in the process is obtaining the correct density of oxide in the tubes during the filling process. Too dense packing will cause subsequent bursting of the tube when the PbO_2 is converted to lead sulfate. The occurrence of this bursting of tubes has been one of the principal objections to the use of tubular plates. Another has been the fact that rates of discharge as high as those obtainable in flat, pasted plates are not possible.

We obtained samples of tubular plates, from a manufacturer of such plates, that had been made from four different oxide blends, soaked in acid for different lengths of time, and at different temperatures. Samples under each of these conditions were examined after 1, 4, 10 and 100 cycles, in order to determine what changes took place in the active material, how these compared with pasted plates and, if possible, to determine the mechanism that caused bursting of the tubes.

This examination was very informative. As in the case of the flat, pasted plates, it was found that, regardless of what initial treatment or type of oxide mix was used, the active material changed to a coralloid structure after a few cycles. As in the case of the flat plates, this seemed to develop first at the outside of the pellet and progress toward the center with increasing number of cycles.

Since the active material was confined within the woven fiberglass tubes and unable to wash out as sediment, or to expand the tube, this conversion from what had at first been a compact and apparently non-porous structure to the open and large pored coralloid had probably been made possible by compacting a large amount of PbO_2 , even more densely within the branches of the coralloid structure. The most intriguing feature of this investigation, however, was the determination that this highly porous spongelike mass was capable of busting the woven fiberglass shell and porous plastic backing strip that together formed the retaining tube in which the active mass was confined.

This indicated not only that the coralloid structure had a great deal more rigidity than we had suspected, but was also capable of growing and expanding with a very large force. A review examination of a number of samples from cycled flat pasted plates revealed that these had also expanded somewhat during cycling.

Even though it does not appear that the coralloid structure is desirable, it is obvious that it can be expected to develop under all conditions and for this reason, if no other, its study should be continued. In addition, it presents other puzzling characteristics that, if understood, might contribute to a more durable battery. Although x-ray analysis and electron microscopy indicate that the individual crystals of PbO_2 are very small, the coralloid structure indicates a dendritic type of growth on a much larger scale, which appears inconsistent with the crystals' small size. What is the mechanism that causes these tiny crystals to group together into compact chains that not only adhere together to form a definite and rigid coralloid structure but also forces them to continue growing against the restrictions imposed by the tubular shell, that itself possesses remarkable strength?

As yet we have been unable to explain the forces that arrange the PbO_2 particles in this manner, but the need for further study should be obvious because the bonding together of the PbO_2 particles is essential for continued cohesion and prevention of shedding. Also, if means can be found to modify the structure of the coralloid so that the cross sections of its branches can be reduced to a somewhat smaller dimension and the pores made more interconnecting, then this might then become the ideal structure that it at first appeared to be. It has already been determined that in lead-calcium alloy plates, the branch dimensions become larger. Although this appears to be a step in the wrong direction, it does show that the coralloid structure can be modified.

EFFECT ON STRUCTURE OF RATE, OR PERTURBATIONS IN RATE, OF CHARGE AND DISCHARGE

The importance of studying the microstructure under different modes of operation and at different stages in electrode life cannot be over-emphasized. The performance of the battery is intimately related to the crystal morphology and the kinetics of reaction can be either improved or impaired depending on the size and disposition of the crystals on the surface of the electrode. While it can be readily seen how the structures produced under different conditions are related to performance, it is not at all obvious as to what steps are required to control undesirable changes.

During the cycling of an electrode, there is a constant change in the microstructure of the active material. During discharge, lead sulfate crystals nucleate and grow on the surface of the lead dioxide and the lead dioxide is also dissolving to furnish the ions needed for the continued growth of the lead sulfate crystals. At slow rates of discharge, relatively few lead sulfate crystals appear on the lead dioxide surface and these grow to a relatively large size without interfering with the many free surfaces where the lead dioxide is dissolving. As higher rates are employed, the crystals become smaller and more numerous. At very high rates, the surfaces have such a dense layer of crystals nucleated at the very beginning that the lead dioxide surface becomes covered almost immediately and large areas become isolated from further reaction. In addition, severe concentration gradients are set up that can seriously affect the pH in certain areas and there is the possibility that basic sulfates rather than normal sulfate will be formed. A further complication is that, as the rate increases, resistance in the active material becomes an increasingly important factor so that conducting paths through the remaining PbO_2 become very essential. Unfortunately, the higher the discharge rate that is employed, the more uneven becomes the current distribution and the greater the probability that these conducting paths will be destroyed by unequal reaction at different points. The above mentioned are only a few of the effects that are rate dependent and while the foregoing discussion applied to the positive plate, similar effects are occurring in the negative.

Although the mechanism of crystal growth is somewhat different in the case of charging, the charging rate can also affect the crystal structure. It is also likely that a following charge or discharge will be influenced by the prior discharge or charge when rates are varied greatly, so that the cell may be said to have a "memory" for prior treatment. It is equally evident that changes in rate during charge or discharge may have an effect, possibly changing the crystal habit, increasing the nucleation rate, etc.

The reactivity of lead dioxide seems to be linked to the presence of a disordered lattice structure, and a similar disordered structure

would seem to be desirable for the lead sulfate. High rates of reaction favor the formation of disordered lattice structure and the incorporation of foreign ions. Thus, a high rate of discharge would be expected to make the subsequent charge more efficient and a high rate of charge should make the subsequent discharge more efficient.

We would also like to determine what effect rate has on the coraloid structure.

For these and other reasons, we have arranged for the Mobility Equipment Research and Development Command at Fort Belvoir (MERADCOM) to prepare batteries for us under conditions that will furnish the required information. MERADCOM has one of the most sophisticated programmable cycling facilities in the country, capable of handling and switching very high currents. The first group of batteries have been placed on test and we expect very shortly to have samples from this group for examination.

INVESTIGATION OF ELECTROCHEMICALLY ACTIVE AND INACTIVE FORMS OF PbO_2

Lead dioxide is a very unique material. Not only does it exist in several polymorphs but it also exhibits differences in electrochemical reactivity. As regards resistance, lead dioxide occupies a position intermediate between metals and insulators. Its resistance is close to the value of $1 \text{ to } 3 \times 10^{-4} \text{ ohm-cm}$ (8, 9). With this value, it has a much lower resistance than most chemical compounds and lower than most semiconductors. Comparing it with other components in the battery, lead has a value of $.2 \times 10^{-4} \text{ ohm-cm}$, while sulfuric acid (1.200 sp. gr.) has a resistance of 1.2 ohm-cm . In this regard, it is worth noting that Thomas (8) reported a resistivity of $74 \times 10^{-4} \text{ ohm-cm}$ for electrochemically formed storage battery PbO_2 , in its usual porous form as it occurs in the battery, whereas, he reported a value of 142×10^{-4} for C. P. chemically prepared PbO_2 , even when compressed to 10 tons/sq. in., which indicates a higher resistance for the chemically prepared form, and is in agreement with our findings as to the relatively unreactive nature of the latter material.

The behavior of the lead-acid battery is in general determined by the kinetics of electrochemical reduction or oxidation of solid and insoluble PbO_2 and PbSO_4 . Two mechanisms are involved in these processes: an electronic mechanism and the mechanism by which metal ions enter into solution and become oxidized or reduced at the conducting components of the plate. The electronic mechanism has been used to explain the reduction of PbO_2 , which has an appreciable conductivity, while reduction of PbSO_4 , a poor conductor, has been explained by the second mechanism.

When a conductor is placed in an electrical field, there are four different charged species that can move. These are anions, cations, electrons and electron holes. The sum of the ionic and electronic conductivities represents the total conductivity.

In the case of lead dioxide, the species that move appear to be electrons. Lead dioxide is a n-type semiconductor with an electronic configuration that suggests that the conduction bands are formed from s-orbitals rather than from unfilled inner orbitals. The conduction band of PbO_2 is due to the 6s levels of the Pb^{4+} ions and is contributed to by the 2p levels of the O^{2-} ions.

There are several possibilities for the presence of free electrons in PbO_2 : the presence of impurities, incorporation of hydrogen and deviation from stoichiometry.

In the case of PbO_2 , high concentrations of dopants are required before significant changes in the carrier concentration occur, indicating that the effect of impurities (other than hydrogen) would not be significant. Unlike compounds like SnO_2 , it has been shown that 3- or 5-valent ions do not influence conductivity in PbO_2 to any great extent.

A number of investigators (10-13) have reported appreciable quantities of bound hydrogen in electrodeposited PbO_2 . However, the presence of hydrogen does not seem to be necessary to explain PbO_2 conductivity, as sputtered PbO_2 films, containing no hydrogen, still had a high carrier density (9).

Values from $\text{PbO}_{1.90}$ to $\text{PbO}_{1.95}$ have been reported for the non-stoichiometry of PbO_2 (14-17). Such a condition could result in a deficiency of at least two oxygen atoms for each four electrons, or alternatively, there could be at least one additional lead atom which is dissociated into a tetravalent lead ion and four electrons.

From the structure of PbO_2 , it might appear that the deficiency in oxygen resulted from the presence of interstitial Pb^{4+} ions which could exist without causing appreciable distortion of the lattice. X-ray diffraction studies of PbO_2 have been made that showed that O_2 could be removed from PbO_2 by treating at temperatures above 140°C in vacuum, without a phase change, down to a composition of $\text{PbO}_{1.90}$ and with a progressive increase in lattice constant values as oxygen was removed. This would seem to be consistent with the presence of excess lead in interstitial positions in the lattice.

On the other hand, the observations that the density of electrodeposited PbO_2 is lower than the x-ray value and that oxygen appears to have a high mobility in PbO_2 (17) would seem to indicate that oxygen vacancies are responsible for the nonstoichiometry of this oxide.

The carrier concentration of $1.4 \times 10^{21} \text{ cm}^{-3}$ found (9) for $\alpha\text{-PbO}_2$ films corresponds to a composition of $\text{PbO}_{1.971}$ if electrons are due only to ionized oxygen vacancies and to $\text{PbO}_{1.942}(\text{OH})_{0.058}$ if they are the result of OH groups substituting for oxygen, as has been suggested (10).

Present chemical analytical methods are not sufficiently exact to distinguish between these two cases. Our studies with nuclear magnetic resonance spectroscopy have revealed relaxation curves with three different slopes, two representing different types of bound water, and the third as yet not completely identified.

The electron density distribution in a crystal represents the structure and is expressible in terms of the amplitudes and phases of the waves diffracted by the various planar segments in the crystal. X-ray structure analysis is usually obtained by the use of relatively large single crystals. The various polymorphs of lead, as naturally occurring in the active material, are extremely small and efforts to grow larger crystals have been unsuccessful. Another problem involves the necessity of determining the lattice positions of the O and H atoms in relation to such a heavy atom as lead. Even with powder samples, however, it is now possible to obtain direct structural information (6).

Between the bonding information obtainable from the use of nuclear magnetic resonance spectroscopy and that obtainable from the nuclear diffraction structural analysis, we are hopeful that answers will be obtained to these problems and that the cause of the electrochemical inactivity in PbO_2 can be pinpointed.

As has been already pointed out in previous reports, progress must of necessity be slow. Extensive calculations are required, that even with computer assistance are very time consuming. The need for neutron diffraction analysis, and the fact that the needed equipment is not a captive facility of NRL, involves inevitable delays even with the best possible scheduling. Unexpected impurities in what had been thought to be pure samples have necessitated re-runs.

However, progress continues to be made, and one theory, that there was an amorphous polymorph of lead dioxide in battery active material, has definitely been refuted.

STUDY OF PLATES CYCLED WITH Pb-Sb VS. Pb-Ca GRIDS

It is a well known fact that the positive active material supported on grids containing antimony has a different physical appearance and physical properties than does active material on grids without antimony. It has been known for a long time that unconfined plates with grids of lead-antimony cycle longer than do plates made with grids of lead alone, lead-calcium or lead-calcium-tin alloys. In addition, lead-antimony alloys are more easily cast, are easier to handle because of their rigidity and corrode more uniformly, as a rule, than do other alloys. In these attributes, leadantimony alloys are beneficial, but their use also promotes a lowered overvoltage at the negative, increased decomposition of the water of the electrolyte and a very definite possibility of

poisoning of personnel from stibine, all of which are undesirable characteristics. For these reasons and also because of the pronounced trend toward maintenance-free vehicles, there is a strong effort being made to reduce or eliminate antimony in grid alloys. At the same time, it becomes necessary to define the reasons for the beneficial action of antimony and to establish the minimum quantity that can be used in alloy without losing this benefit.

For this study, we obtained battery plates from four different manufacturers with various percentages of antimony in the grid alloy and also with lead-calcium and lead-calcium-tin alloy in the grids. The plates with different alloys were all cycled similarly and plates removed for examination at predetermined points regulated by the remaining capacity. With this procedure, we hoped to obtain plates at the same point of failure in each case, even though the total number of cycles on each plate might be quite different. These samples have been prepared for microscopic examination and examined carefully by both optical and scanning electron microscopy.

Although we have not yet finished with examination, we have found no correlation between microstructure and retained capacity. While it is obvious in some cases that the loss of capacity is related to active material softening or a less cohesive microstructure, in other cases the retention of microstructure cohesion has been very good but an equal loss of capacity has occurred. There seems to be a correlation between loss of capacity and loss of contact of the active material with the grid bars. There is evidence that the expansion of the coralloid structure referred to in a previous section may tend to enlarge the ring defined by the grid wire circumference and cause the active material to lose contact. There is also considerable difference in the extent of corrosion in the different alloys, and this is also a possible source of loss of capacity unrelated to the plate microstructure.

It is now evident that there are several factors that combined or singly are responsible for capacity loss. We have been unable to trace any structure that is recognizable as being caused by the presence of antimony, either by optical or electron scanning microscopy. It is possible that by the use of transmission electron microscopy we may be able to find microstructure in very small crystal that can be related to the presence or absence of antimony (20), but such differences are not visible at the levels of magnification presently possible with the scanning electron microscope in use here.

We had hoped that the image analyzer would be of assistance in differentiating between the microstructure of these different active materials, but the interconnected nature of the microstructure confuses the particle area counts and makes difficult correct determination of void space relative to active material or the determination of particle shape.

We are still working on these various problems and we hope to be able to eventually correlate all of the confusing factors. One point that is fairly obvious, however, is that the plates of the different manufacturers are failing for different reasons, irrespective of the type of grid. This may explain some of the conflicting ideas that have been expressed as to the cause of battery failure. It also raises interesting questions, since it would seem that there is very little real difference in the procedures used for preparing plates by the different manufacturers, so what is responsible for the quite different mode of failure that we observe? Why does one active material shed severely during cycling, while another shows very little change, even when the same grid alloy is used. It is precisely in this area that we intend to use our best procedures for trace element analysis and structure analysis, to seek for an answer.

PROPOSED WORK FOR 1979

The principal goal of this investigation is to improve the performance of the lead-acid battery. This can be done by accomplishing one or more of the following: increasing the utilization of the active material, preventing the gradual decrease of capacity that accompanies cycling, prolonging the useful battery life, increasing the charging rate and making available higher current densities for discharge. As a matter of fact, these objectives are interrelated and improvement in one may well improve one or more of the others.

INCREASING THE UTILIZATION OF THE ACTIVE MATERIAL

The principal cause of poor active material utilization, according to our investigations is the fact that in the initial formation, a portion of the lead dioxide does not have electrochemical activity and that after cycling the portion having no electrochemical activity tends to increase. We have determined that the active portion appears to have not only a disordered atomic structure but incorporates hydrogen in some form, perhaps as an OH radical. The electron density of the active form is also higher than that of the inactive form.

We have begun an investigation, with the cooperation of NRL's Laboratory for the Structure of Matter, to determine the position of hydrogen atoms in the electrochemically active material. By the use of sophisticated x-ray and neutron diffraction techniques as well as nuclear magnetic resonance spectroscopy, we hope to define the structure of the electrochemically active form and the effect of impurities on the atomic structure. Once this is determined, there is the possibility of stabilizing this structure by the use of the proper dopants.

In the original work which used low resolution neutron diffraction, it was expected that there would be sufficiently large differences in structural parameters of new and failed plates to make possible the extraction of the necessary data from the radial distribution function by profile refinement methods. However, we did not obtain sufficiently large structural changes between the new and failed plates to make it possible to sufficiently define the changes that take place during cycling. For this reason, we have resorted to high resolution neutron diffraction to be able to detect much smaller structural changes. The low resolution neutron diffraction did enable us to determine, from the background intensity, changes in the hydrogen concentration but it was not sufficiently accurate to develop structural data.

It should be noted that NRL's Laboratory for the Structure of Matter is donating its services practically free of charge, a considerable contribution. One scientist is devoting about one half of his time to this project and others are contributing consulting services. There are also charges for computer time and for the service of the neutron diffraction facility that are being borne by this group. Under this DOE

contract, we are furnishing the necessary samples, performing the necessary chemical analysis, nuclear magnetic resonance spectroscopy and similar services required in connection with this structural determination.

INVESTIGATION OF STRUCTURAL CHANGES BOTH FROM REPEATED CYCLING AND FROM CHANGES IN CURRENT DENSITY

It has been pointed out that crystal growth is a function of current density. The higher the current density the greater becomes the number of crystal nuclei and the smaller the individual crystals. The number and packing of the crystals affect diffusion rates as well as surface area. High rates increase the possibility of stratification.

We have already begun a study of the effect of current density on a laboratory scale, but these results only approximate what may occur in the industrial battery. In order to determine what can be expected under service conditions, it is necessary to study industrial batteries that have been subjected to various charge-discharge regimes and perturbations in rates of discharge. We do not have the facilities for handling the necessary high currents for such a study at NRL so this work has been subcontracted to the MERADCOM Group at Fort Belvoir where one of the finest facilities for programmed switching of very high currents is available. Cells are now being cycled in this facility under different current density variations and we will be examining these in the coming year.

This is another case where extra personnel are being used without direct cost. Even though a subcontract of \$15K has been given to the MERADCOM Group, we are getting far more than this in return. Not only do we obtain the use of the equipment but the personnel to operate it. Even the batteries are being furnished as a spin-off of some of their own work. In addition, facilities are being provided where we can disassemble the cells and take care of the preliminary preparation of samples, so that it is not necessary to transport the entire batteries back and forth between the two agencies.

STUDY OF CORALLOID STRUCTURE

The coralloid structure develops after a few cycles in all types of lead-acid battery plates, tubular and pasted. The coralloid structure apparently ties up a considerable portion of the lead dioxide in a dense, non-porous form that is not able to react. In all other respects, the coralloid structure would seem to be desirable. The formation of the coralloid structure will be studied closely in an attempt to find means to reduce its structure to smaller dimensions. That is to say, to reduce the branches of the coralloid structure to a smaller diameter by electrochemical or chemical treatment. The approximate size needed can be determined from the negative plate. When no expanders are used in the negative active material, the lead dendrites strongly resemble, in size and shape, the dimensions of the coralloid structure observed in the positive.

It has been found that when the dendrites are of this diameter, the lead sulfate becomes of a thickness sufficient to cause passivation before all of the lead is converted to lead sulfate, resulting in poor utilization of the active material. If an expander is used, the lead dendrites are of a smaller size and, in this case, the lead is completely converted to lead sulfate before the lead sulfate film is thick enough to cause passivation.

Presumably, the same thickness of lead sulfate becomes passivating in the positive, so that a coralloid structure of the dimensions of the lead dendrites formed when an organic expander is used in the negative active material should insure full utilization of the lead dioxide.

This would require only a 50% reduction in the coralloid dimensions now being formed. Although an organic expander, unfortunately, cannot be used in the positive active material, it is possible that an inorganic material might accomplish the same purpose.

The development of the coralloid structure is possible because the small individual crystals of PbO_2 are in some manner brought together in long chains to form a dense cohesive network of high strength and conductivity. This is a very unusual process and if it could be more fully understood might enable us to prevent the softening and shedding that occurs when plates are cycled. For these reasons, the formation of the coralloid will be followed at each step by optical and electron microscopy in an attempt to learn the factors controlling its development.

STUDY OF THE CHARACTERISTICS OF TUBULAR PLATES

There are several reasons that a study of tubular plates is desirable. In the first place, there is only one manufacturer in this country making tubular plates. There has been very little published information about this type of plate and none at all concerning the properties of the active material. Secondly, the method of manufacture is quite different, yet after cycling the product seems to be the same as for the flat plate. This raises the question whether the long time spent in the curing step for the flat plates is really necessary. We plan to study the reactions that take place while the tubular plate is soaked and formed to see how much they resemble those produced by mixing and curing. Third, the use of tubular plates, where the active material is restrained by the porous tube, gives a means of studying the formation of the coralloid structure more easily than in the case of flat plates, because the structure lasts longer before shedding begins. Fourth, the comparison of the two types of plate through the various steps of manufacture and use may furnish valuable information that would not be revealed by studying either alone.

Two manufacturers have been approached and have expressed their willingness to furnish plates for this type of experiment. Since there was only one manufacturer of such plates in the U.S.A., the other material comes from overseas.

DETERMINATION OF THE ROLE PLAYED BY ANTIMONY IN THE ACTIVE MATERIAL

We have amassed a large number of plates containing grids without antimony or with antimony in various amounts. These have been obtained from several manufacturers and range from those that have been formed only to those that have been cycled for various lengths of time up to complete failure. Samples have been prepared from all of these plates and have been studied by optical and scanning electron microscopy. While considerable information has been obtained from this study, the exact role of antimony has not been determined. The study will be extended to include other types of instrumentation in order to determine more conclusively the manner in which these various materials differ, and how antimony is incorporated into the structure.

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